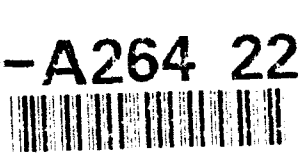
AD-A264 220



(2)

DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a REPORT SECURITY CLASSIFICATION Unclassified	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release and sale; distribution unlimited.
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Report #24	5 MONITORING ORGANIZATION REPORT NUMBER(S) 4135010
6a NAME OF PERFORMING ORGANIZATION University of Minnesota 6b OFFICE SYMBOL (If applicable) ONR	7a NAME OF MONITORING ORGANIZATION Office of Naval Research
6c ADDRESS (City, State, and ZIP Code) Department of Chemistry 207 Pleasant St. SE Minneapolis, MN 55455-0431	7b ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217-5000
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research 8b OFFICE SYMBOL (If applicable) ONR	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N001489J1301
8c ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 2217-5000	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO: 61153N; PROJECT NO: 4135; TASK NO:; WORK UNIT ACCESSION NO: 4135010

11 TITLE (Include Security Classification)
"Design of Acentric Materials: X-ray Structures of Guanidinium *p*-Nitro- and *p*-Hydroxybenzenesulfonate" (Unclassified)

12 PERSONAL AUTHOR(S)
Russell, V.A.; Etter, M.C.; Ward, M.D.

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Technical	FROM 6/1/92 TO 5/31/93	April 22, 1993	7

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	guanidinium sulfonate/second-harmonic generation/ hydrogen bonding/materials design
07	03		

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Guanidinium *p*-nitro- and *p*-hydroxybenzenesulfonate crystallize in noncentrosymmetric (acentric) space groups and exhibit second-harmonic generation. The engineering of these structures was accomplished using hydrogen bonding and the tendency to pack in centrosymmetric structures overcome by screening of the dipolar forces between arylsulfonates by charged layers of guanidinium ions.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL Harold E. Guard	22b TELEPHONE (Include Area Code) (202) 646-4311 22c OFFICE SYMBOL ONR Code 1113

DD Form 1473, JUN 86 — Previous editions are obsolete — SECURITY CLASSIFICATION OF THIS PAGE

S/N 0102-LF-014-6603 — Unclassified

OFFICE OF NAVAL RESEARCH

Grant or Contract N001489J1301

R&T Code 4135010

Technical Report #24

"Design of Acentric Materials: X-ray Structures of Guanidinium *p*-Nitro- and *p*-Hydroxybenzenesulfonate"

by

V.A. Russell, M.C. Etter, and M.D. Ward

University of Minnesota
Department of Chemistry
Minneapolis, MN

April 22, 1993

In previous work we found that the hydrogen-bond sheet pattern (Figure 1) occurs frequently in salts of guanidinium with simple alkyl and aryl sulfonates. Our study of the solid-state behavior of guanidinium sulfonates continues with investigation of guanidinium salts of sulfonates having other potential hydrogen-bonding groups. The focus of this report are the X-ray structures of two guanidinium sulfonate salts that crystallize in noncentrosymmetric space groups and exhibit second-harmonic generation: guanidinium *p*-nitrobenzenesulfonate and guanidinium *p*-hydroxybenzenesulfonate. The former salt has a hydrogen-bond motif similar to that found previously in other guanidinium sulfonate salts, while the latter lacks two of the six hydrogen bonds typical of these structures. Weak interactions between the nitro or hydroxyl group and guanidinium ion are suggested by the crystal structures. Segregation of the cations and anions into distinct regions may be responsible for the formation of noncentrosymmetric lattices. Inspection of the crystal structures reveals that the arylsulfonates are organized into layers separated by charged layers of guanidinium ions. This suggests that the formation of a noncentrosymmetric lattice is due to screening of the dipolar forces between the arylsulfonates. The anions would otherwise tend to self-assemble with anti-parallel alignment of molecular dipoles and subsequently form a centrosymmetric phase.

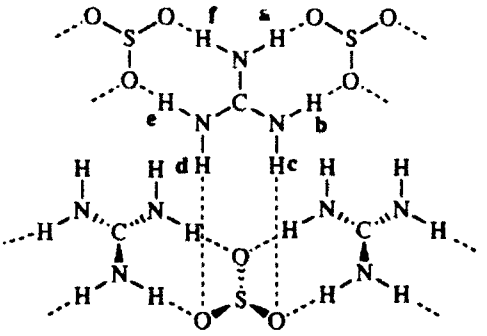
The X-ray crystal data for guanidinium *p*-nitrobenzenesulfonate follows: $C_7H_{10}N_4O_5S$, $M_r = 262.24$, orthorhombic, *Ama*2, $a = 7.471$ (8), $b = 20.690$ (7), $c = 7.340$ (2) Å, $V = 1135$ (2) Å^3, $Z = 4$, $D_{calc} = 1.535$ g/cm^3, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 2.89$ cm^{-1}, $F(000) = 544$, $T = 297$ K, $R = 0.048$, $R_w = 0.047$ for 1165 observed reflections. The structure is composed of sheets of *p*-nitrobenzenesulfonate anions in the *bc* plane linked by guanidinium sulfonate hydrogen-bonding interactions. The nitro group and one sulfonate oxygen atom are coplanar with the aromatic ring. The anion layers are related by two-fold axes and A-centering; each anion layer is offset from neighboring layers by about 90°. The X-ray structure of guanidinium *p*-hydroxybenzenesulfonate is similar, but is body-centered rather than *A*-centered. X-ray data follows: $C_7H_{11}N_3O_4S$, $M_r = 233.24$, orthorhombic, *Ima*2, $a = 7.191$ (4), $b = 17.345$ (5), $c = 7.899$ (3) Å, $V = 985$ (1) Å^3, $Z = 4$, $D_x = 1.572$ g/cm^3, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 3.13$ cm^{-1}, $F(000) = 488$, $T = 297$ K, $R = 0.035$, $R_w = 0.047$ for 635 unique observed reflections. As in guanidinium *p*-nitrobenzenesulfonate the structure is composed of sheets of anions linked by hydrogen bonding. Stereoviews of the crystal packing each salt are given in Figures 2 and 3.

Hydrogen-bond geometries of both salts are given in Table I. The hydrogen bonding in guanidinium *p*-nitrobenzenesulfonate is slightly different than predicted. We expected this salt to crystallize with hydrogen-bond sheets (Figure 1) arranged in bilayers, as found in guanidinium *p*-toluenesulfonate, due to the relatively poor accepting ability of the nitro oxygens compared to the sulfonate oxygens. We found, however, that a different hydrogen bond pattern occurs in this structure. Hydrogen-bonded ribbons of four guanidinium-sulfonate hydrogen-bond interactions identical to those found in previous structures occur in guanidinium *p*-nitrobenzenesulfonate. Each ribbon is linked to a neighboring ribbon through two similar guanidinium sulfonate hydrogen bonds; i.e. the two remaining guanidinium protons interact with the two remaining oxygen lone pairs with the guanidinium ion approximately perpendicular to the plane of the three sulfonate oxygens on a neighboring ribbon, rather than in approximately the same plane as in guanidinium *p*-toluenesulfonate. These six interactions make up a distorted hydrogen-bonded single layer structure in the *z*-direction (see Figure 2). Hydrogen bonding to nitro groups does not occur although there may be a weak bifurcated interaction between one nitro oxygen atom and two mirror-related guanidinium protons attached to the same nitrogen atom, with N...O 3.192 (6) and H...O 2.90 (3) Å.

In guanidinium *p*-hydroxybenzenesulfonate hydrogen-bonded ribbons of four guanidinium-sulfonate hydrogen bonds occur as in guanidinium *p*-nitrobenzenesulfonate. The ribbons are not linked to one another through hydrogen bonding, however. Although the hydroxyl proton was not found in the X-ray analysis, it seems to be located in a position to maximize a number of weak interactions. A bifurcated weak interaction takes place between the phenolic oxygen atom and the remaining two guanidinium protons of length $N\ldots O_{hydroxy}$ = 3.188 (4) Å and angle 139.71°. No hydrogen bonding occurs between the remaining sulfonate oxygens and the hydroxy proton as evidenced by no O...O distances less than 3.6 Å. An arrangement similar to the single layer structure found in the *p*-nitrobenzenesulfonate salt can be seen in the *c*-direction. The difference in guanidinium-sulfonate hydrogen bonding in this structure compared to the fully hydrogen-bonded pattern found in previous structures results from competitive hydrogen bonding with the hydroxyl group. The hydroxyl proton is a better hydrogen bond donor than guanidinium proton and so would be expected to hydrogen bond to the best acceptor (sulfonate oxygen) as per our general hydrogen bond rule of best donor hydrogen bonding to best acceptor.

Both structures are noncentrosymmetric with all nitro or hydroxyl groups oriented in one direction. Both exhibit second harmonic generation, guanidinium *p*-nitrobenzenesulfonate about 0.75 x urea and guanidinium *p*-hydroxybenzenesulfonate about 0.5 x urea. We have successfully engineered the structures of these two salts into noncentrosymmetric arrangements using hydrogen bonding interactions. Our findings will be applied to the design of other novel noncentrosymmetric molecular materials.

Table I. Hydrogen Bond Geometries in Guanidinium *p*-Nitro- and *p*-Hydroxybenzenesulfonate.



hydrogen bond	guanidinium *p*-nitrobenzenesulfonate N...O distance (Å)	N-H...O angle (°)	guanidinium *p*-hydroxybenzenesulfonate N...O distance (Å)	N-H...O angle (°)
a	2.900 (4)	177.48	2.938 (4)	174.49
b	3.005 (5)	174.26	2.955 (3)	168.81
c	3.018 (4)	169.21	> 3.6	
d	= c	= c	= c	= c
e	= b	= b	= b	= b
f	= a	= a		

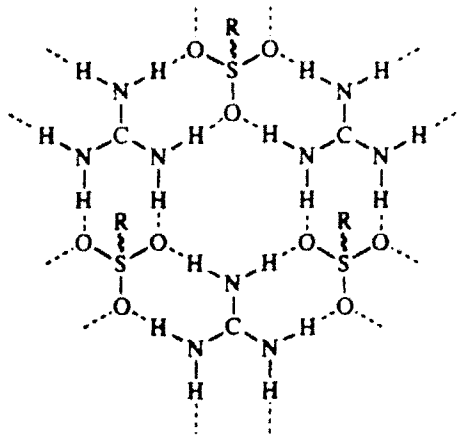


Figure 1. Common hydrogen-bond pattern in guanidinium sulfonates.

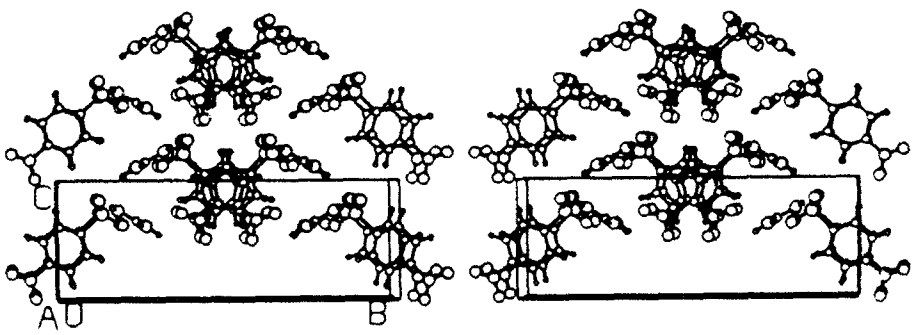


Figure 2. Stereoview along the *x*-axis in guanidinium *p*-nitrobenzenesulfonate.

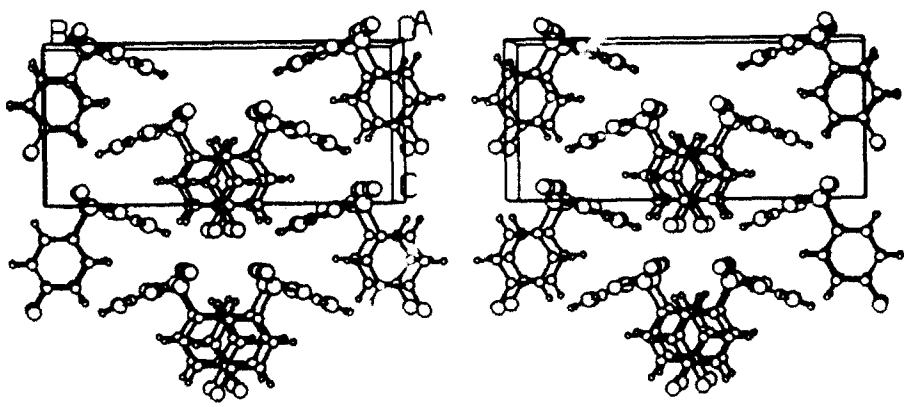


Figure 3. Stereoview along the *x*-axis in guanidinium *p*-hydroxybenzenesulfonate.

ORGANIC CHEMISTRY & MOLECULAR RECOGNITION - Distribution List

Professor O.T. Beachley, Jr.
Department of Chemistry
State University of New York
Buffalo, NY 14214

Dr. Alan Berry
Chemistry Division, Code 6120
Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5000

Professor Jerald S. Bradshaw
Department of Chemistry
Brigham Young University
Provo, UT 84602
R&T Code 413p002

Professor Ronald Breslow
Department of Chemistry
Columbia University
New York, NY 10027
R&T Code 413p005

Dr. Duncan W. Brown
Advanced Technology Materials, Inc.
520-B Danbury Road
New Milford, CT 06776

Professor Herbert C. Brown
Purdue University
Department of Chemistry
West Lafayette, IN 47907

Professor Steven L. Buchwald
Department of Chemistry
Massachusetts Institute of Tech
Cambridge, MA 02139

Professor Cynthia J. Burrows
Department of Chemistry
State University of New York at
Stony Brook
Stony Brook, NY 11794-3400

Dr. Roque J. Calvo
Executive Secretary
The Electrochemical Society
10 South Main Street
Pennington, NJ 08534-2896

Professor Peter Chen
Department of Chemistry
Harvard University
Cambridge, MA 02138

Professor N. John Cooper
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

Professor Anthony W. Czarnik
Department of Chemistry
Ohio State University
120 West 18th Avenue
Columbus, OH 43210-1173

Professor Peter Dervan
Department of Chemistry
California Institute of Technology
Pasadena, CA 91125

Professor Francois N. Diederich
Department of Chemistry
University of California
405 Hilgard Avenue
Los Angeles, CA 90024

Professor Dennis A. Dougherty
Department of Chemistry
California Institute of Technology
Pasadena, CA 91125

Professor Kenneth M. Doxsee
Department of Chemistry
University of Oregon
Eugene, OR 97403

Dr. Regis J. Ebner, Jr.
Director of Finance
Materials Research Society
9800 McKnight Road, Suite #27
Pittsburgh, PA 15237

Professor Margaret C. Etter
Department of Chemistry
University of Minnesota
207 Pleasant Street, S.E.
Minneapolis, MN 55455

Professor Wilmer K. Fife
Department of Chemistry
Indiana University
1125 East 38th Street
P.O. Box 647
Indianapolis, IN 46223

Professor Samuel H. Gellman
Department of Chemistry
University of Wisconsin
Madison, WI 53706

Professor Andrew D. Hamilton
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

Prof. Mark J. Hampden-Smith
Department of Chemistry
University of New Mexico
Albuquerque, NM 87131

Professor William E. Hatfield
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514

Dr. Kelvin Higa
Chemistry Division
Research Department
Naval Weapons Center
China Lake, CA 93555

Professor Kenneth D. Karlin
Merryman Hall 146
The Johns Hopkins University
34th & Charles Streets
Baltimore, MD 21218

Professor Arthur E. Martell
Department of Chemistry
Texas A&M University
College Station, TX 77843-3255

Professor Thomas J. McCarthy
Department of Polymer Science
University of Massachusetts
Room 701 Graduate Research Center
Amherst, MA 01003
R&T Code 400x015

Dr. Stephen W. McElvany
Code 6113, Chemistry Division
Naval Research Laboratory
Washington, DC 20375-5000

Professor Lisa McElwee-White
Department of Chemistry
The Leland Stanford Junior Univ.
Stanford, CA 94305

Professor Theordore G. Pavlopoulos
Naval Ocean Systems Center
Code 521 (B-111)
San Diego, CA 92152-5000

Professor William S. Rees, Jr.
Chemistry Division
The Florida State University
Tallahassee, FL 32306-3006

Professor Peter Schultz
Department of Chemistry
University of California
Berkeley, CA 94720
R&T Code 413j005

Dr. Alok Singh
Ctr. for Bio/Molec. Science Eng.
Department of the Navy
Naval Research Lab., Code 6090
Washingotn, DC 20375-5000

Dr. Michael L. Sinnott
Unviersity of Brisol
School of Chemistry
Cantock's Close
Briston, England BS8 1TS

Dr. Timothy M. Swager
Departmentof Chemistry
University of Pennsylvania
Philadelphia, PA 19104-6323

Professor Richard L. Wells
Department of Chemistry
Duke University
Durham, NC 27706

Professor Jeffrey D. Winkler
Department of Chemistry
The University of Chicago
5735 S. Ellis Avenue
Chicago, IL 60637

Professor Jeffrey D. Zubkowski
Department of Chemistry
Jackson State University
P.O. Box 17910, 1400 Lynch St.
Jackson, MS 39217